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PATENT APPLICATION

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**APPLICATION FOR
UNITED STATES LETTERS PATENT**

TO ALL WHOM IT MAY CONCERN:

Be it known that WE, Hany Aziz, Nan-Xing Hu, Zoran D. Popovic, and James M. Duff, have invented

OLEDs HAVING LIGHT ABSORBING ELECTRODE

OLEDs HAVING LIGHT ABSORBING ELECTRODE

BACKGROUND OF THE INVENTION

Organic light emitting devices (OLEDs) represent a promising technology for display applications. A typical organic light emitting device includes a transparent first electrode, which usually acts as a hole-injecting anode; a luminescent region comprising one or more electroluminescent organic layer(s); and a second electrode (also called a "back electrode"), which usually acts as an electron-injecting cathode. In order to facilitate electron injection from the back electrode into the electroluminescent layer(s), the back electrode generally is formed of a low work function metal, and therefore is highly reflective. When a voltage is applied across the first and second electrodes, light is emitted from the electroluminescent layer(s) and through the transparent anode. When viewed under high ambient illumination, the reflective back electrode reflects a substantial amount of the ambient illumination to the observer, which results in higher ratios of reflected illumination as compared to the device's own emission, which results in "washout" of the displayed image.

In order to improve the contrast of electroluminescent displays in general, light absorbing layers as described, for example, in U.S. Patent 4,287,449, or optical interference members as described, for example, in U.S. Patent 5,049,780, have been used to reduce the ambient illumination reflection. Both of these approaches involve the use of optical films made of materials that are generally non-conductive. These properties limit the applicability of such materials to organic light emitting devices, which, unlike inorganic electroluminescent phosphor devices, require the direct injection of charges from the electrodes to the electroluminescent layer(s). In addition, the fabrication of such optical films, essentially from dielectric inorganic materials, often requires the use of sputtering or electron beam evaporation techniques. These fabrication techniques require additional instrumentation to be incorporated into the otherwise relatively simple fabrication process of organic light emitting devices by thermal evaporation or spin coating techniques. Also, in cases using optical interference effects for achieving improved contrast, such as disclosed, for example, in U.S. Patent 5,049,780, it is usually required to use more than one optical film in order to achieve the desired improvement, which is disadvantageous to the fabrication

process. Furthermore, the resulting improvement in display contrast is inevitably dependent on the viewing angle.

Thus, there is a need, addressed by the present invention, for new OLEDs that avoid or minimize a number of the disadvantages described above for conventional electroluminescent devices.

Organic light emitting devices are disclosed in the following:

Pending US Serial No. 09/800,716 (titled "cathodes for electroluminescent devices having improved contrast and reduced dark spot growth"), assigned to Xerox Corporation; and

O. Renault et al., "A low reflectivity multilayer cathode for organic light-emitting diodes," *Thin Solid Films*, Vol. 379, pp. 195-198 (December 8, 2000);

International Application Publication No. WO 01/08240 A1; and

David Johnson et al., "Contrast Enhancement of OLED Displays," http://www.luxell.com/pdfs/OLED_tech_ppr.pdf, pp. 1-3 (April 2001).

SUMMARY OF THE INVENTION

The present invention is accomplished in embodiments by providing an organic light emitting device comprising:

a first electrode;

a second electrode; and

a luminescent region including an organic electroluminescent material between the first electrode and the second electrode, wherein one of the first electrode and the second electrode includes both a substantially transparent charge injecting layer adjacent to the luminescent region and an electrically conductive light absorbing layer.

There is also provided in embodiments an organic light emitting device comprising in sequence:

(a) a cathode including:

(i) an electrically conductive light absorbing layer, and

(ii) a substantially transparent electron injecting layer;

(b) a luminescent region including an organic electroluminescent material; and

(c) an anode that is substantially transparent to light.

There is provided in additional embodiments an organic light emitting device comprising in sequence:

(a) a cathode that is substantially transparent to light;

(b) a luminescent region including an organic electroluminescent material; and

- 1 (c) an anode including:
2 (i) a substantially transparent hole injecting layer, and
3 (ii) an electrically conductive light absorbing layer.
4

5 **BRIEF DESCRIPTION OF THE DRAWINGS**

6
7 Other aspects of the present invention will become apparent as the following
8 description proceeds and upon reference to the Figures which represent illustrative
9 embodiments:

10 FIG. 1 is a schematic, elevational view in cross-section of a first embodiment of
11 the present OLED;

12 FIG. 2 is a schematic, elevational view in cross-section of a second embodiment
13 of the present OLED;

14 FIG. 3 is a schematic, elevational view in cross-section of a third embodiment of
15 the present OLED; and

16 FIG. 4 is a schematic, elevational view in cross-section of a fourth embodiment
17 of the present OLED.

18 Unless otherwise noted, the same reference numeral in different Figures refers to
19 the same or similar feature.
20

21 **DETAILED DESCRIPTION**

22
23 The present organic light emitting device is composed of at least a first
24 electrode; a second electrode; and a luminescent region including an organic
25 electroluminescent material between the first electrode and the second electrode,
26 wherein one of the first electrode and the second electrode includes both a substantially
27 transparent charge injecting layer adjacent to the luminescent region and an electrically
28 conductive light absorbing layer. Either the cathode or the anode can include the
29 charge injecting layer and the electrically conductive light absorbing layer. The charge
30 injecting layer may be either an electron injecting layer (in the case of a cathode) or a
31 hole injecting layer (in the case of an anode). The present organic light emitting device
32 may include a substrate either as a separate layer adjacent to one of the electrodes or
33 incorporated into one of the electrodes (e.g., the electrically conductive light absorbing
34 layer that is part of an electrode includes in embodiments a substrate material to result
35 in an electrically conductive light absorbing substrate).

1 A first exemplary embodiment is seen in FIG. 1 where the organic light emitting
2 device 2A is composed of in the depicted sequence: a substrate 4A; an anode 6A; a
3 luminescent region 8A; and a cathode 10A including a substantially transparent
4 electron injecting layer 12A, an optional buffer layer 14A, an electrically conductive
5 light absorbing layer 16A, and an optional metallic layer 18A. In FIG. 1, the anode 6A
6 and substrate 4A are substantially transparent so that light emitted within the
7 luminescent region can reach the viewer.

8 As used herein, the phrase "substantially transparent" indicates a significant level
9 of light transmissivity through a layer such as for example at least about 50%
10 transmissivity, particularly at least about 70% transmissivity.

11 A second exemplary embodiment is seen in FIG. 2 where the organic light
12 emitting device 2B is composed of in the depicted sequence: an anode 6B; a
13 luminescent region 8B; and a cathode 10B including a substantially transparent electron
14 injecting layer 12B, an optional buffer layer 14B, an electrically conductive light
15 absorbing layer 16B, and an optional metallic layer 18B; and a substrate 4B. In FIG. 2,
16 the anode 6B is substantially transparent so that light emitted within the luminescent
17 region can reach the viewer.

18 A third exemplary embodiment is seen in FIG. 3 where the organic light emitting
19 device 2C is composed of in the depicted sequence: a substrate 4C; a cathode 10C; a
20 luminescent region 8C; and an anode 6C including a substantially transparent hole
21 injecting layer 12C, an optional buffer layer 14C, an electrically conductive light
22 absorbing layer 16C, and an optional metallic layer 18C. In FIG. 3, the cathode 10C
23 and substrate 4C are substantially transparent so that light emitted within the
24 luminescent region can reach the viewer.

25 A fourth exemplary embodiment is seen in FIG. 4 where the organic light
26 emitting device 2D is composed of in the depicted sequence: a cathode 10D; a
27 luminescent region 8D; and an anode 6D including a substantially transparent hole
28 injecting layer 12D, an optional buffer layer 14D, an electrically conductive light
29 absorbing layer 16D, and an optional metallic layer 18D; and a substrate 4D. In FIG. 4,
30 the cathode 10D is substantially transparent so that light emitted within the luminescent
31 region can reach the viewer.

32 FIGS. 1-4 depict a single light absorbing layer. In other embodiments, however,
33 two or more light absorbing layers may be present.

34 The reason for improved contrast by the present invention is now discussed. The
35 incorporation of a substantially transparent charge injecting layer (12A, 12B, 12C,

1 12D) results in the transmission of a substantial portion of ambient light reaching this
2 layer, and therefore, the portion of ambient light that is reflected back from this layer to
3 the viewer is substantially reduced. Furthermore, the incorporation of an electrically
4 conductive light absorbing layer (16A, 16B, 16C, 16D) absorbs a substantial portion of
5 the ambient light that is transmitted through the charge injecting layer (and the optional
6 buffer layer), and therefore, a substantial portion of the ambient light that reaches the
7 optional metallic layer is not reflected back to the viewer, and hence image washout is
8 substantially reduced.

9 The amount of light absorption of the light absorbing layer depends on the
10 extinction coefficient of the light absorbing material comprising the light absorbing
11 layer, as well as on the thickness of the light absorbing layer, where, in general, a
12 higher value for the extinction coefficient and a larger layer thickness lead to more light
13 absorption, and hence are more desirable in embodiments. Also, the higher the
14 extinction coefficient of the material, the less the thickness needed to achieve a certain
15 amount of light absorption.

16 The multi-layer electrode of the present OLED (having the charge injecting
17 layer and the electrically conductive light absorbing layer) exhibits as a whole both
18 lateral electrical conductivity (across the width of the electrode) and cross directional
19 electrical conductivity (through the thickness of the electrode). However, in certain
20 embodiments, a layer of the multi-layer electrode such as the optional buffer layer, may
21 exhibit cross directional conductivity but not lateral conductivity. That each of the
22 electrode layers is considered part of the electrode arises from the fact that each of (1)
23 the charge injecting layer, (2) the electrically conductive light absorbing layer, and the
24 (3) the optional protective metallic layer contribute to both lateral conduction and cross
25 directional conduction. The optional buffer layer, being made of an insulative material,
26 does not contribute to lateral conduction, but is considered part of the electrode because
27 if the buffer layer is thin enough, it can sustain cross directional conduction. In
28 embodiments of the present invention, the multi-layer electrode is a stack of adjacent
29 layers where each layer exhibits a cross directional electrical conductivity with an
30 ohmic resistance less than about 100 ohms, particularly less than about 10 ohms, and
31 especially less than about 1 ohm.

32 A substantially transparent substrate can comprise various suitable materials
33 including, for example, polymeric components, glass, quartz and the like. Suitable
34 polymeric components include, but are not limited to polyesters such as MYLAR[®],
35 polycarbonates, polyacrylates, polymethacrylates, polysulfones, and the like. Other

1 substrate materials can also be selected provided, for example, that the materials can
2 effectively support the other layers, and do not interfere with the device functional
3 performance.

4 An opaque substrate can comprise various suitable materials including, for
5 example, polymeric components like polyesters such as MYLAR[®], polycarbonates,
6 polyacrylates, polymethacrylates, polysulfones, and the like, which contain coloring
7 agents or dyes such as carbon black. The substrate can also be comprised of
8 silicon such as amorphous silicon, polycrystalline silicon, single crystal silicon, and the
9 like. Another class of materials that can be used in the substrate are ceramics such as
10 metallic compounds like metal oxides, halides, hydroxides, sulfides and others.

11 The substrate may have a thickness ranging for example from about 10 to about
12 5,000 micrometers, and more particularly from about 25 to about 1,000 micrometers.

13 A substantially transparent anode (such as that used in the OLED devices of
14 FIGS. 1-2) can comprise suitable positive charge injecting materials such as indium tin
15 oxide (ITO), silicon, tin oxide, and metals with a work function ranging from about 4
16 eV to about 6 eV such as gold, platinum, and palladium. Other suitable materials for
17 the anode include, but are not limited to, electrically conductive carbon, π -conjugated
18 polymers such as polyaniline, polythiophene, polypyrrole, and the like having, for
19 example, a work function equal to, or greater than, about 4 eV, and particularly from
20 about 4 eV to about 6 eV. A substantially transparent anode can comprise very thin
21 substantially transparent metallic layers, comprising a metal with a work function
22 ranging from about 4 eV to about 6 eV such as gold, palladium and the like, having a
23 thickness, for example, from about 10 Å to about 200 Å, and, particularly, from about
24 30 Å to about 100 Å. Additional suitable forms of the anode are disclosed in U.S.
25 Patents 4,885,211 and 5,703,436, which are incorporated herein by reference in their
26 entirety.

27 The thickness of the substantially transparent anode can range from about 10 Å to
28 about 50,000 Å, with the preferred range depending on the optical constants of the
29 anode material. One illustrative range of anode thickness is from about 300 Å to about
30 3,000 Å. Of course, a thickness outside of this range can also be used.

31 A substantially transparent cathode (such as that used in the OLED devices of
32 FIGS. 3-4) can comprise very thin substantially transparent metallic layers comprising
33 a metal with a work function ranging from about 2 eV to about 4 eV, such as Mg, Ag,
34 Al, Ca, In, Li and their alloys such as Mg:Ag alloys, comprised of, for example, from
35 about 80 to 95 volume percent of Mg and about 20 to about 5 volume percent of Ag,

1 and Li:Al alloys, comprised of, for example, from about 90 to 99 volume percent of Al,
2 and from about 10 to about 1 volume percent of Li, and the like, having a thickness,
3 for example, from about 10 Å to about 200 Å, and, particularly, from about 30 Å to
4 about 100 Å. Other substantially transparent cathodes are disclosed in US Serial No.
5 09/800,716, cited earlier, and incorporated herein by reference in its entirety, such as
6 cathodes comprising a layer, of thickness from about 100 Å to about 10,000 Å, and
7 particularly from about 500 Å to about 5,000 Å, comprised of a metal, an organic
8 material, and a third component which can be a metal, an organic material, or any other
9 material. One embodiment is a cathode composed of a layer comprised of about 47.4
10 volume percent of Mg, about 5.2 volume percent of Ag, and about 47.4 volume percent
11 of tris(8-hydroxyquinoline) aluminum (AlQ₃). Additional suitable forms of
12 substantially transparent cathodes are disclosed in U.S. Patent 5,703,436, which is
13 incorporated herein by reference in its entirety.

14 The thickness of the substantially transparent cathode can range from about 10 Å
15 to about 50,000 Å, with the preferred range depending on the optical constants of the
16 cathode material. One illustrative range of cathode thickness is from about 30 Å to
17 about 100 Å. Another illustrative range is from about 50 Å to about 500 Å. Of course,
18 a thickness outside of this range can also be used.

19 A substantially transparent electron injecting layer can include very thin
20 substantially transparent metallic layers, composed of a metal with a work function
21 ranging from about 2 eV to about 4 eV, such as Mg, Ag, Al, Ca, In, Li and their alloys
22 such as Mg:Ag alloys composed of, for example, from about 80 to 95 volume percent
23 of Mg and about 20 to about 5 volume percent of Ag, and Li:Al alloys, composed of,
24 for example, from about 90 to 99 volume percent of Al, and from about 10 to about 1
25 volume percent of Li, and the like, having a thickness, for example, from about 10 Å to
26 about 200 Å, and, particularly, from about 30 Å to about 100 Å. Other substantially
27 transparent electron injecting layers are disclosed in US Serial No. 09/800,716, cited
28 earlier, and incorporated herein by reference in its entirety, such as a layer, of
29 thickness from about 100 Å to about 10,000 Å, and particularly from about 500 Å to
30 about 5,000 Å, comprised of a metal, an organic material, and a third component which
31 can be a metal, an organic material, or any other material. One embodiment is a layer
32 composed of about 47.4 volume percent of Mg, about 5.2 volume percent of Ag, and
33 about 47.4 volume percent of tris(8-hydroxyquinoline) aluminum (AlQ₃).

34 The thickness of a substantially transparent electron injecting layer can range
35 from about 10 Å to about 50,000 Å, with the preferred range depending on the optical

1 constants of the cathode material. One illustrative range of thickness of the electron
2 injecting layer is from about 30 Å to about 100 Å. Another illustrative range is from
3 about 50 Å to about 500 Å. Of course, a thickness outside of this range can also be
4 used.

5 A substantially transparent hole injecting layer can be composed of suitable
6 positive charge injecting materials such as indium tin oxide (ITO), silicon, tin oxide,
7 and metals with a work function ranging from about 4 eV to about 6 eV, such as, gold,
8 platinum, and palladium. Other suitable materials for the hole injecting layer include,
9 but are not limited to, electrically conductive carbon, π -conjugated polymers such as
10 polyaniline, polythiophene, polypyrrole, and the like having, for example, a work
11 function equal to, or greater than, about 4 eV, and particularly from about 4 eV to about
12 6 eV. A substantially transparent hole injecting material can be composed of very thin
13 substantially transparent metallic layers, comprising a metal with a work function
14 ranging from about 4 eV to about 6 eV, such as gold, palladium and the like, having a
15 thickness, for example, from about 10 Å to about 200 Å, and, particularly, from about
16 30 Å to about 100 Å. Additional suitable forms of hole injecting layers are disclosed in
17 U.S. Patents 4,885,211 and 5,703,436, which are incorporated herein by reference in
18 their entirety.

19 The thickness of a substantially transparent hole injecting layer can range, for
20 example, from about 10 Å to about 50,000 Å, with the preferred range depending on
21 the optical constants of the selected material. One illustrative range of thickness of the
22 hole injecting layer is from about 30 Å to about 100 Å. Another illustrative range is
23 from about 50 Å to about 500 Å. Of course, a thickness outside of this range can also
24 be used.

25 Where the charge injecting layer and the light absorbing layer may undesirably
26 react with one another if the two layers are in contact, or where the charge injecting
27 layer may be damaged during coating of the light absorbing layer on it, thereby
28 degrading the performance of the organic light emitting device, the presence of an
29 intervening buffer layer will prevent or minimize such reactions or damage. A buffer
30 layer, therefore, will include a material that may not undesirably react with both the
31 charge injecting layer and the light absorbing layer, and also that may protect the charge
32 injecting layer from possible damage during coating of the light absorbing layer on it.
33 Examples of materials that can be selected to comprise the buffer layer are metallic
34 compounds such as metal oxides like Al_2O_3 , metal halides like MgF_2 , and others.
35 Other materials that can be selected to form the buffer layer include porphyrins like

1 metal phthalocyanine such as copper phthalocyanine. Preferred materials that can be
2 used include SiO, SiO₂ or mixtures thereof. The buffer layer is preferably non-
3 reflective. In embodiments, the buffer layer is partially or substantially transparent
4 and/or light absorbing.

5 The thickness of the buffer layer is selected depending on the materials used to
6 form this buffer layer such that significant cross directional conduction from the
7 electrically conductive light absorbing layer to the charge injecting layer across the
8 buffer layer is not interrupted by the buffer layer. Typically, the thickness of the buffer
9 layer can range from about 10 Å to about 5,000 Å, particularly from about 50 Å to
10 about 1,000 Å.

11 The electrically conductive light absorbing layer can include a single material
12 that combines the desired light absorption and electrical conduction properties such as
13 carbon (e.g., graphite and C₆₀), Si, Ge and the like, a metal such as Mo, Ni, Cr, Pd, V,
14 Se, In and their alloys such as INCONEL™, NICHROME™, and the like, or a
15 conductive light absorbing metal oxide. The electrically conductive light absorbing
16 layer can also be comprised of a blend of two or more materials, wherein at least one of
17 the materials is a light absorbing material such as an organic dye or pigment, such as a
18 phthalocyanine, a perinone, a perylene, a perylene dimer, and the like, and wherein one
19 of the materials is a conductive material, such as a metal like Ag, Al, Au, Cu, Mg, In
20 and the like. When the light absorbing layer is comprised of two or more materials, the
21 concentration of each material in the layer can be adjusted in order to obtain the desired
22 electrical conduction and light absorption properties. For example, the layer can
23 comprise from about 50 volume percent to about 99 volume percent of a light
24 absorbing material and from about 50 volume percent to about 1 volume percent of an
25 electrically conductive material.

26 The electrically conductive light absorbing layer may have a thickness ranging
27 for example from about 10 Å to about 10,000 Å, where preferred ranges for the
28 thickness can be selected depending on the materials used in forming the layer. One
29 illustrative thickness range is from about 10 Å to about 500 Å. Another illustrative
30 thickness range is from about 500 Å to about 5,000 Å. Yet, another illustrative
31 thickness range is from about 5,000 Å to about 10,000 Å. Of course, a thickness
32 outside of these ranges can also be used.

33 The phrase "light absorbing" indicates noticeable extinction of light, for example,
34 at least about 50% extinction of light entering the light absorbing layer, particularly at
35 least about 90% extinction of light entering the light absorbing layer. The light

1 absorbing layer functions on a different principle from that of an optical interference
2 layer. The light absorbing layer relies on light absorption, whereas the optical
3 interference layer relies on destructive light interference. Thus, the light absorbing
4 layer achieves a noticeable extinction of light without relying on destructive light
5 interference.

6 In embodiments, the ohmic resistance for cross directional conduction across the
7 light absorbing layer does not exceed an illustrative value of about 100 ohms; in
8 particular, the ohmic resistance does not exceed another illustrative value of about 10
9 ohms; in embodiments, the ohmic resistance does not exceed still another illustrative
10 value of about 1 ohm.

11 Where the collective sheet resistance of the charge injecting layer and the
12 electrically conductive light absorbing layer is too high to sustain significant lateral
13 conduction, such as if the collective sheet resistance of the charge injecting layer and
14 the electrically conductive light absorbing layer exceeds an illustrative value of about 5
15 ohms per square, or if the light absorbing layer (or any layers underneath it) is degraded
16 as a result of exposure to external environment thereby degrading the performance of
17 the organic light emitting device, a protective metallic layer coated on the light
18 absorbing layer can be used to lower the sheet resistance of the electrode containing the
19 light absorbing layer or to prevent (or at least reduce) the damage caused to the device
20 by the external environment.

21 The optional metallic layer can be composed of any suitable metal such as Ag,
22 Au, Al, Mg, In, Ca, Sr and the like, or alloys thereof such as Mg:Ag alloys composed
23 of, for example, from about 80 to 95 volume percent of Mg and about 20 to about 5
24 volume percent of Ag, and Li:Al alloys, composed of, for example, from about 90 to 99
25 volume percent of Al, and from about 10 to about 1 volume percent of Li.

26 The optional metallic layer preferably is thick enough in order to achieve a
27 reduced sheet resistance such as less than about 5 ohms per square, and particularly
28 even less than about 1 ohm per square, and also preferably is thick enough to
29 effectively isolate the light absorbing layer from external environment. However, there
30 is no particular upper limit for the thickness except as may be required by device
31 fabrication considerations. Typically, the metallic layer may have a thickness ranging
32 for example from about 100 Å to about 10,000 Å, and more particularly from about
33 1,000 Å to about 4,000 Å. Of course, a thickness outside of these ranges can also be
34 used.

1 The luminescent region is composed of an organic electroluminescent material.
2 Electroluminescent materials include, for example, polyphenylenevinylenes such as
3 poly(p-phenylenevinylene) PPV, poly(2-methoxy-5-(2-ethylhexyloxy)1,4-
4 phenylenevinylene) MEHPPV and poly(2,5-dialkoxyphenylenevinylene) PDMeOPV,
5 and other materials disclosed in U.S Patent 5,247,190, which is incorporated herein by
6 reference in its entirety; polyphenylenes, such as poly(p-phenylene) PPP, ladder-poly-
7 *para*-phenylene (LPPP), and poly(tetrahydropyrene) PTHP; and polyfluorenes, such as
8 poly(9,9-di-n-octylfluorene-2,7-diyl), poly(2,8-(6,7,12,12-tetraalkylindenofluorene)
9 and copolymers containing fluorenes such as fluorene-amine copolymers (see e.g.,
10 Bernius et al., "Developmental Progress of Electroluminescent Polymeric Materials
11 and Devices," Proceedings of SPIE Conference on Organic Light Emitting Materials
12 and Devices III, Denver, Colorado, July 1999, Volume 3797, p. 129).

13 Another class of organic electroluminescent materials that can be utilized in the
14 luminescent region includes, but is not limited to, the metal oxinoid compounds as
15 disclosed in U.S. Patents 4,539,507; 5,151,629; 5,150,006; 5,141,671 and 5,846,666,
16 each incorporated herein by reference in its entirety. Illustrative examples include
17 tris(8-hydroxyquinolate) aluminum (AlQ3), which is one preferred example, and
18 bis(8-hydroxyquinolato)-(4-phenylphenolato) aluminum (BALq) which is another
19 preferred example. Other examples of this class of materials include tris(8-
20 hydroxyquinolate) gallium, bis(8-hydroxyquinolate) magnesium, bis(8-
21 hydroxyquinolate) zinc, tris(5-methyl-8-hydroxyquinolate) aluminum, tris(7-
22 propyl-8-quinolinolato) aluminum, bis[benzo{f}-8-quinolate]zinc, bis(10-
23 hydroxybenzo[h]quinolate) beryllium, and the like, and metal thioxinoid compounds
24 disclosed in U.S. Patent 5,846,666 (which is incorporated herein by reference in its
25 entirety), such as metal thioxinoid compounds of bis(8-quinolinethiolato)zinc, bis(8-
26 quinolinethiolato)cadmium, tris(8-quinolinethiolato)gallium, tris(8-
27 quinolinethiolato)indium, bis(5-methylquinolinethiolato)zinc, tris(5-
28 methylquinolinethiolato)gallium, tris(5-methylquinolinethiolato)indium, bis(5-
29 methylquinolinethiolato)cadmium, bis(3-methylquinolinethiolato)cadmium, bis(5-
30 methylquinolinethiolato)zinc, bis[benzo{f}-8-quinolinethiolato]zinc, bis[3-
31 methylbenzo{f}-8-quinolinethiolato]zinc, bis[3,7-dimethylbenzo{f}-8-
32 quinolinethiolato]zinc, and the like. Preferred materials are bis(8-
33 quinolinethiolato)zinc, bis(8-quinolinethiolato)cadmium, tris(8-
34 quinolinethiolato)gallium, tris(8-quinolinethiolato)indium and bis[benzo{f}-8-
35 quinolinethiolato]zinc.

1 More specifically, a class of organic electroluminescent materials that can be
2 used in the luminescent region comprises stilbene derivatives, such as those disclosed
3 in U.S. Patent 5,516,577, incorporated herein by reference in its entirety. A preferred
4 stilbene derivative is 4,4'-bis(2,2-diphenylvinyl)biphenyl.

5 Another class of suitable organic electroluminescent materials suitable for
6 utilizing in the luminescent region is the oxadiazole metal chelates. These materials
7 include bis[2-(2-hydroxyphenyl)-5-phenyl-1,3,4-oxadiazolato]zinc; bis[2-(2-
8 hydroxyphenyl)-5-phenyl-1,3,4-oxadiazolato]beryllium; bis[2-(2-hydroxyphenyl)-5-(1-
9 naphthyl)-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-(1-naphthyl)-1,3,4-
10 oxadiazolato]beryllium; bis[5-biphenyl-2-(2-hydroxyphenyl)-1,3,4-oxadiazolato]zinc;
11 bis[5-biphenyl-2-(2-hydroxyphenyl)-1,3,4-oxadiazolato]beryllium; bis(2-
12 hydroxyphenyl)-5-phenyl-1,3,4-oxadiazolato]lithium; bis[2-(2-hydroxyphenyl)-5-p-
13 tolyl-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-p-tolyl-1,3,4-
14 oxadiazolato]beryllium; bis[5-(p-tert-butylphenyl)-2-(2-hydroxyphenyl)-1,3,4-
15 oxadiazolato]zinc; bis[5-(p-tert-butylphenyl)-2-(2-hydroxyphenyl)-1,3,4-
16 oxadiazolato]beryllium; bis[2-(2-hydroxyphenyl)-5-(3-fluorophenyl)-1,3,4-
17 oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-(4-fluorophenyl)-1,3,4-
18 oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-(4-fluorophenyl)-1,3,4-
19 oxadiazolato]beryllium; bis[5-(4-chlorophenyl)-2-(2-hydroxyphenyl)-1,3,4-
20 oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-(4-methoxyphenyl)-1,3,4-
21 oxadiazolato]zinc; bis[2-(2-hydroxy-4-methylphenyl)-5-phenyl-1,3,4-
22 oxadiazolato]zinc; bis[2- α -(2-hydroxynaphthyl)-5-phenyl-1,3,4-oxadiazolato]zinc;
23 bis[2-(2-hydroxyphenyl)-5-p-pyridyl-1,3,4-oxadiazolato]zinc; bis[2-(2-
24 hydroxyphenyl)-5-p-pyridyl-1,3,4-oxadiazolato]beryllium; bis[2-(2-hydroxyphenyl)-5-
25 (2-thiophenyl)-1,3,4-oxadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-phenyl-1,3,4-
26 thiadiazolato]zinc; bis[2-(2-hydroxyphenyl)-5-phenyl-1,3,4-thiadiazolato]beryllium;
27 bis[2-(2-hydroxyphenyl)-5-(1-naphthyl)-1,3,4-thiadiazolato]zinc; and bis[2-(2-
28 hydroxyphenyl)-5-(1-naphthyl)-1,3,4-thiadiazolato]beryllium, and the like; and the
29 triazines including those disclosed in U.S. Patent 6,057,048, which is incorporated
30 herein by reference in its entirety.

31 The luminescent region can further include from about 0.01 weight percent to
32 about 25 weight percent of a luminescent material as a dopant. Examples of dopant
33 materials that can be utilized in the luminescent region are fluorescent materials, such
34 as coumarin, dicyanomethylene pyranes, polymethine, oxabenzanthrane, xanthene,
35 pyrylium, carbostyl, perylene, and the like. Another preferred class of fluorescent

1 materials are quinacridone dyes. Illustrative examples of quinacridone dyes include
2 quinacridone, 2-methylquinacridone, 2,9-dimethylquinacridone, 2-chloroquinacridone,
3 2-fluoroquinacridone, 1,2-benzoquinacridone, N,N'-dimethylquinacridone, N,N'-
4 dimethyl-2-methylquinacridone, N,N'-dimethyl-2,9-dimethylquinacridone, N,N'-
5 dimethyl-2-chloroquinacridone, N,N'-dimethyl-2-fluoroquinacridone, N,N'-dimethyl-
6 1,2-benzoquinacridone, and the like as disclosed in U.S. Patents 5,227,252; 5,276,381
7 and 5,593,788, each incorporated herein by reference in its entirety. Another class of
8 fluorescent materials that may be used is fused ring fluorescent dyes. Exemplary
9 suitable fused ring fluorescent dyes include perylene, rubrene, anthracene, coronene,
10 phenanthrene, pyrene and the like, as disclosed in U.S. Patent 3,172,862, which is
11 incorporated herein by reference in its entirety. Also, fluorescent materials include
12 butadienes, such as 1,4-diphenylbutadiene and tetraphenylbutadiene, and stilbenes, and
13 the like, as disclosed in U.S. Patents 4,356,429 and 5,516,577, each incorporated herein
14 by reference in its entirety. Other examples of fluorescent materials that can be used
15 are those disclosed in U.S. Patent 5,601,903, which is incorporated herein by reference
16 in its entirety.

17 Additionally, luminescent dopants that can be utilized in the luminescent region
18 are the fluorescent dyes disclosed in U.S. Patent 5,935,720 (which is incorporated
19 herein by reference in its entirety) such as 4-(dicyanomethylene)-2-*I-propyl*-6-(1,1,7,7-
20 tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTb); the lanthanide metal chelate
21 complexes, such as for example, tris(acetylacetonato)(phenanthroline) terbium,
22 tris(acetylacetonato)(phenanthroline) europium, and tris(thenoyl
23 trifluoroacetato)(phenanthroline) europium, and those disclosed in Kido et al.,
24 "White light emitting organic electroluminescent device using lanthanide complexes,"
25 Jpn. J. Appl. Phys., Volume 35, pp. L394-L396 (1996), which is incorporated herein by
26 reference in its entirety; and phosphorescent materials, such as organometallic
27 compounds containing heavy metal atoms that lead to strong spin-orbit coupling, such
28 as those disclosed in Baldo et.al., "Highly efficient organic phosphorescent emission
29 from organic electroluminescent devices," Letters to Nature, Volume 395, pp. 151-154
30 (1998), which is incorporated herein by reference in its entirety. Preferred examples
31 include 2,3,7,8,12,13,17,18-octaethyl-21*H*23*H*-phorpine platinum(II) (PtOEP) and *fac*
32 tris(2-phenylpyridine)iridium (Ir(ppy)₃).

33 The luminescent region can also include one or more materials with hole-
34 transporting properties. Examples of hole-transporting materials that can be utilized in
35 the luminescent region include polypyrrole, polyaniline, poly(phenylene vinylene),

polythiophene, polyarylamine as disclosed in U.S. Patent 5,728,801, which is incorporated herein by reference in its entirety, and their derivatives, and known semiconductive organic materials; porphyrin derivatives such as 1,10,15,20-tetraphenyl-21H,23H-porphyrin copper (II) disclosed in U.S. Patent 4,356,429, incorporated herein by reference in its entirety; copper phthalocyanine, copper tetramethyl phthalocyanine; zinc phthalocyanine; titanium oxide phthalocyanine; magnesium phthalocyanine; and the like

A specific class of hole transporting materials that can be utilized in the luminescent region are the aromatic tertiary amines such as those disclosed in U.S. Patent 4,539,507, which is incorporated herein by reference in its entirety. Suitable exemplary aromatic tertiary amines include, but are not limited to, bis(4-dimethylamino-2-methylphenyl)phenylmethane, N,N,N-tri(p-tolyl)amine, 1,1-bis(4-di-p-tolylaminophenyl)cyclohexane, 1,1-bis(4-di-p-tolylaminophenyl)-4-phenyl cyclohexane, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine, N,N'-diphenyl-N,N'-bis(4-methoxyphenyl)-1,1'-biphenyl-4,4'-diamine, N,N,N',N'-tetra-p-tolyl-1,1'-biphenyl-4,4'-diamine, N,N'-di-1-naphthyl-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine, mixtures thereof and the like. Another class of aromatic tertiary amines are polynuclear aromatic amines. Examples of these polynuclear aromatic amines include, but are not limited to, N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenyl]aniline; N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenyl]-m-toluidine; N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenyl]-p-toluidine; N,N-bis-[4'-(N-phenyl-N-p-tolylamino)-4-biphenyl]aniline; N,N-bis-[4'-(N-phenyl-N-p-tolylamino)-4-biphenyl]-m-toluidine; N,N-bis-[4'-(N-phenyl-N-p-tolylamino)-4-biphenyl]-p-toluidine; N,N-bis-[4'-(N-phenyl-N-p-chlorophenylamino)-4-biphenyl]-m-toluidine; N,N-bis-[4'-(N-phenyl-N-m-chlorophenylamino)-4-biphenyl]-m-toluidine; N,N-bis-[4'-(N-phenyl-N-m-chlorophenylamino)-4-biphenyl]-p-toluidine; N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenyl]-p-chloroaniline; N,N-bis-[4'-(N-phenyl-N-p-tolylamino)-4-biphenyl]-m-chloroaniline; N,N-bis-[4'-(N-phenyl-N-m-tolylamino)-4-biphenyl]-1-aminonaphthalene, mixtures thereof and the like; 4,4'-bis(9-carbazolyl)-1,1'-biphenyl compounds, such as 4,4'-bis(9-carbazolyl)-1,1'-biphenyl and 4,4'-bis(3-methyl-9-carbazolyl)-1,1'-biphenyl, and the like.

A specific class of the hole transporting materials that can be used in the luminescent region are the indolo-carabazoles, such as those disclosed in U.S. Patents 5,942,340 and 5,952,115, each incorporated herein by reference in its entirety, such as

1 5,11-di-naphthyl-5,11-dihydroindolo[3,2-b]carbazole, and 2,8-dimethyl-5,11-di-
2 naphthyl-5,11-dihydroindolo[3,2-b]carbazole; N,N,N',N'-tetraarylbenzidines, wherein
3 aryl may be selected from phenyl, m-tolyl, p-tolyl, m-methoxyphenyl, p-
4 methoxyphenyl, 1-naphthyl, 2-naphthyl and the like. Illustrative examples of
5 N,N,N',N'-tetraarylbenzidine are N,N'-di-1-naphthyl -N,N'- diphenyl-1,1'-biphenyl-4,4'-
6 diamine, which is more preferred; N,N'-bis(3-methylphenyl) -N,N'- diphenyl-1,1'-
7 biphenyl-4,4'-diamine; N,N'-bis(3-methoxyphenyl) -N,N'- diphenyl-1,1'-biphenyl-4,4'-
8 diamine, and the like. Preferred hole transporting materials that can be used in the
9 luminescent region are the naphthyl-substituted benzidine derivatives.

10 The luminescent region can also include one or more materials with electron
11 transporting properties. An example of electron transporting materials that can be
12 utilized in the luminescent region is polyfluorenes, such as poly(9,9-di-n-octylfluorene-
13 2,7-diyl), poly(2,8-(6,7,12,12-tetraalkylindenofluorene) and copolymers containing
14 fluorenes such as fluorene-amine copolymers, as disclosed in incorporated Bernius et
15 al., Proceedings of SPIE Conference on Organic Light Emitting Materials and Devices
16 III, Denver, Colorado, July 1999, Volume 3797, p. 129.

17 Other examples of electron transporting materials that can be utilized in the
18 luminescent region can be selected from the metal oxinoid compounds, the oxadiazole
19 metal chelate compounds, the triazine compounds and the stilbene compounds,
20 examples of which have been described above in detail.

21 In embodiments where the luminescent region includes one or more hole
22 transport material and/or one or more electron transport material in addition to the
23 organic electroluminescent material(s), the organic electroluminescent material, the
24 hole transport material(s), and/or the electron transport material(s) can be formed in
25 separate regions, such as the OLEDs disclosed in U.S. Patents 4,539,507; 4,720,432
26 and 4,769,292; or in the same region thus forming mixed regions of two or more
27 materials, such as the OLEDs disclosed in U.S. Patent 6,130,001, and in U.S.
28 Application Serial Nos. 09/357,551, filed on July 20, 1999; 09/606,670, filed on June
29 30, 2000; and 09/770,159, filed on January 26, 2001. The disclosures of these patents
30 and patent applications are incorporated herein by reference in their entirety.

31 The thickness of the luminescent region can vary for example, from about 10 Å
32 to about 10,000 Å, typically from about 200 Å to about 2,000 Å, and particularly from
33 about 500 Å to about 1,500 Å. In embodiments wherein the luminescent region
34 includes two or more layers, the thickness of each layer can, for example, be from

1 about 10 Å to about 5,000 Å, typically from about 50 Å to about 2,000 Å, and
2 particularly from about 100 Å to about 1,500 Å.

3 The organic light emitting device can be fabricated by sequentially forming the
4 layers comprising the organic light emitting device on the substrate, using any suitable
5 thin film forming technique, typically, spin coating or deposition by thermal
6 evaporation in vacuum. In embodiments, the charge injecting layer, the light
7 absorbing layer, and the optional buffer layer and metallic layer are deposited by
8 thermal evaporation in vacuum.

9 More details about fabrication and operation of organic light emitting devices are
10 disclosed, for example, in U.S. Patents 4,539,507 and 4,769,292, and in copending
11 U.S. Applications No. 09/357,551, filed on July 20, 1999; No. 09/606,670, filed on
12 June 30, 2000; and No. 09/770,159, filed on January 26, 2001, the disclosure of each
13 patent and patent application being totally incorporated herein by reference.

14 The invention will now be described in detail with respect to specific preferred
15 embodiments thereof, it being understood that these examples are intended to be
16 illustrative only and the invention is not intended to be limited to the materials,
17 conditions, or process parameters recited herein. All percentages and parts are by
18 weight unless otherwise indicated.

19 20 EXAMPLE

21
22 An inventive organic light emitting device according to the device structure of
23 FIG. 1 was fabricated. The organic light emitting device was composed of in the
24 sequence:

- 25 a substrate made of glass of about 1 mm thickness;
- 26 an anode composed of indium tin oxide of about 200 nm thickness;
- 27 a luminescent region composed of a hole transport layer of thickness about 60 nm
28 coated on the anode, made of *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenyl-benzidine
29 (NPB), and a luminescent electron transport layer, about 75 nm thick, coated on the
30 hole transport layer made of tris (8-hydroxyquinoline) aluminum (AlQ3); and
- 31 a cathode including: (a) a substantially transparent electron injecting layer, about
32 4 nm thick, made of Mg:Ag alloy (9:1 by volume), (b) a buffer layer, about 200 nm
33 thick, made of SiO, (c) a light absorbing layer, about 500 nm thick, made of a black
34 pigment material, Bis (1,8-Naphthimidazo) perinone, and (d) a metallic layer, about
35 200 nm thick, made of Ag.

1
2 COMPARATIVE EXAMPLE
3

4 A comparative organic light emitting device, similar to the inventive OLED of
5 the Example but which included a conventional cathode, was fabricated and evaluated.
6 The organic light emitting device was composed of in the sequence:

7 a substrate made of glass of thickness about 1 mm;

8 an anode composed of indium tin oxide, of thickness about 200 nm;

9 a luminescent region, composed of a hole transport layer of thickness about 60
10 nm coated on the anode, made of *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenyl-benzidine
11 (NPB), and a luminescent electron transport layer, about 75 nm thick, coated on the
12 hole transport layer made of tris (8-hydroxyquinoline) aluminum (AlQ3); and

13 a cathode including: (a) an electron injecting layer, about 120 nm thick, made of
14 Mg:Ag alloy (9:1 by volume); and (b) a metallic layer, about 80 nm thick, made of Ag.

15 Both the inventive and comparative organic light emitting devices including the
16 cathode layers were fabricated by thermal evaporation in vacuum (about 5×10^{-6} torr.) in
17 the same pump down cycle.

18 Visual examination of the inventive and comparative organic light emitting
19 devices revealed negligible reflectivity of the cathode of the inventive organic light
20 emitting device, whereas the cathode of the comparative organic light emitting device
21 was highly reflective of ambient illumination, giving it a mirror-like appearance.

22 When operated under 7 volts, emission from the inventive organic light emitting
23 device demonstrated excellent visibility, regardless of the viewing angle, even when
24 viewed under strong ambient illumination from a 200W flood light source placed about
25 15 cms apart from the device. On the other hand, emission from the comparative
26 organic light emitting device, when operated under 7 volts, was almost invisible under
27 the same ambient illumination conditions.

28 Other modifications of the present invention may occur to those skilled in the
29 art based upon a reading of the present disclosure and these modifications are
30 intended to be included within the scope of the present invention.